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C32 COPPER COMPLEXES WITH BIOLOGICALLY SIGNIFICANT LIGANDS:RAPID KINETIC AND THERMODYNAMIC EQUILIBRIUM STUDY OF THE Cu(II) COMPLEXES WITH GLUTATHIONE, L-CYSTEINE AND D-PENICILLAMINE.

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The anaerobic reactions of Cu(II) with glutathione(GSH) and related thioles have been studied by fast reaction kinetic techniques. It showed the presence of intermediate(s) in the reaction pathway. Previous studies on the Cu(II) thiole system was hampered by formation of polymeric solid Cu(I) thiole species, in this study the pH of GSH was raised to 11.0 before mixing and this eliminated solid formation. The first order rate constant for complex formation was 23.9 s^{-1} for GSH and 5.4 s^{-1} for D-pencilamine. In all cases the decay of the intermediate followed a bi-exponantail path with k_1= 1.40s^{-1} and k_2=0.02 s^{-1} at pH=11.0 and k_1=1.70s^{-1} and k_2=.02s^{-1} at pH=9.0 indicating the presence of more than one intermediate. Indeed the complex spectra was recorded on an *HP photodiode array spectrophotometer with a Hi-Tec rapid kinetic accessor*y , the presence of a rapidly forming species(species **I**)(~ 0.03s after mixing) was evident as an intense peak(λ_{max} = 362 nm , ε= 800 $M^{-1}cm^{-1}$). This species decays to species **II**(absorbs at 300 nm,ε= 600$M^{-1}cm^{-1}$) .Finally, species **II** decays to products. The band at 362 is typical for a Cu$\rightarrow$S charge transfer. The proposed mechanism for anaerobic reduction of Cu(II) by Thiole can be:

$$Cu(II) + GS^- \rightarrow [Cu(II)\text{-- } SG]^+_n \rightarrow [\ Cu(I)\text{--- } \overset{\bullet}{S}G]^+_n$$

(I) (II)

$$2[GS^{\bullet}\text{--}Cu(I)]^+ \rightarrow \ GSSG\ +2Cu(I)$$, GSSG=oxidized glutathione.

The Cu(II) complexes with GSSG were also studied , stoichiometry in solution gave Cu(II)/GSSG ratio 1:1 (λmax =627nm) and a 2:1 complex which absorbs at 590 nm. The effect of pH was studied and visible spectra showed the presence of more than one complex depending on the pH value. some kinetic experiments on the effect of molecular oxygen were performed at pH 9.0 on both GSH and GSSG solutions with Cu(II) and a significant change was observed. K values for Cu(II)/GSSG , GSH and D-penicillamine were found using pH titration data and SUPERQUAD computer program .